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Self-assembly of chiral amphiphiles with π-conjugated tectons

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Self-assembly of chiral amphiphiles with π-conjugated tectons into one-dimensional helical nanostructures offers great potential applications in the biological, physical, and material sciences. In this review, the recent development of supramolecular self-assembly of chiral amphiphiles with π-conjugated tectons has been discussed on the basis of experimental exploration by elegantly utilizing cooperative noncovalent forces such as π–π stacking, hydrophobic interaction, hydrogen bond and electrostatic interaction, and the potential applications of these self-assembled helical nanostructures in chiral recognition, asymmetric catalysis, electrical conduction, switchable interfaces and soft template for the fabrication of one-dimensional hard materials are described by a representative example. Meanwhile, some scientific and technical challenges in the development of supramolecular self-assembly of chiral amphiphiles with π-conjugated tectons are also presented. It is hoped that this review can summarize the strategies for self-assembling soft nanomaterials by using chiral amphiphiles with π-conjugated tectons, and also as a guideline for design functional nanomaterials for various potential applications.

chirality, amphiphiles, self-assembly, helical nanostructures, π-conjugated molecules

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Self-assembly of chiral molecules is a widely observed feature for natural biomacromolecules that directs the formation of highly ordered structures, e.g., the spontaneous self-assembly of DNA into a double helix and assembly of proteins and polysaccharides into α-helices. Inspired by the unique features of fascinating biological superstructures, chemists have been able to design a variety aesthetically appealing helical supramolecular assemblies by elegantly utilizing cooperative noncovalent and covalent forces, such as π–π stacking, hydrogen bonding, solvophobic effects, van der Waals, metal-ligand and chirality [1–9]. In this context, the control of the supramolecular organization of π-conjugated systems into helices of nanoscopic dimensions is of fundamental importance [10–17], as the resulting structures could find application in the emerging area of (supramolecular) electronics and photonics because of their unique electronic and optical properties [18,19].

Among a variety of self-assembling building blocks, amphiphilic molecules with chiral substitutions, such as nucleic acids, proteins, polysaccharides, and phospholipids [20–26], and containing both hydrophilic and hydrophobic parts, forms one category of the most powerful building blocks. When amphiphiles are dispersed in solvent, the hydrophilic component of the amphiphile preferentially interacts with the aqueous or polar phase while the hydrophobic portion tends to reside in the air or in the nonpolar solvent. Therefore, depending on the external environments, molecular structures and shapes, and relative volume fraction of hydrophilic and hydrophobic parts, these molecules are able to self-assemble into a variety of structures with a wide range of dimensionalities, ranging from 0D spherical micelles through 1D cylindrical micelles to extended 2D sheets. Clearly, these different structures have been gaining interest for technological applications, such as nanodevices [27–29], drug delivery [30–33], and template synthesis [34–37], and some also possess distinct material properties,

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such as elasticity.

In contrast to conventional amphiphiles, the chiral amphiphiles with special functional groups are synthesised in recent years [38–47]. The building blocks for these chiral amphiphiles can be either small organic molecules or polymers, and their supramolecular structures, especially one-dimensional helical nanostructures such as nanofibers, nanowires and nanotubes, are constructed on the basis of noncovalent interactions or dynamic covalent bonds [43–45, 47–49]. In these supramolecular nanostructures, the arrangement morphologies of the amphiphile molecules are hierarchical since the dynamic and reversible conformational changes can be triggered by external environments such as temperature, pH and solvent [50–53], which can lead to some functional nanostructures with novel properties. Therefore, advances in the development of new type of chiral amphiphiles will not only enrich the family of conventional amphiphiles that are based on covalent bonds but will also provide a new kind of building block for the preparation of complex self-assemblies. In particular, various examples of chiral molecules with extended π-conjugated ring systems, such as hexabenzocoronenes [54,55], perylene bisimides (PTCDI) [56–58], and oligothiophene [59], porphyrin [60,61] and 1,1′-binaphthyls [62] have been reported to form π-stacks with helical supramolecular structures that exhibit some novel physical and chemical properties.

In this paper, the recent development of supramolecular self-assembly of different type of chiral amphiphiles with π-conjugated tectons is reviewed on the basis of experimental exploration with different noncovalent forces. In addition, the potential applications of these self-assembled supramolecular functional nanostructures are also concisely described as a separate part. It is hoped that this review can summarize the strategies for self-assembling soft nanomaterials by using chiral amphiphiles with π-conjugated tectons, and also as a guideline for design functional nanomaterials for various potential applications.

1 Strategies and experimental explorations towards chiral self-assembly

Non-covalent synthesis is regarded as a kind of self-assembly method that is very useful in the construction of chemical structures with a high degree of structural complexity. One of the advantages of non-covalent is the possibility for dynamic and reversible self-assembly. In the following discussion, the strategies and experimental explorations towards supramolecular nanostructures is summarized by the different type of chiarl amphilphiles. As π-conjugated tectons is the key part for the amiphiphilic molecules discussed in this review paper, the driving force are mainly the cooperative effect of π–π stacking interaction and other non-covalent interactions. Specifically, chiral substitutions normally supply the driving forces for the formation of chiral supramolecular nanostructures by forming preferential handedness hindrance.

1.1 Discotic π-conjugated molecules as tectons

Modifying of polycyclic aromatic hydrocarbons (i.e. discotic molecules) by using chiral substitutions is a general strategy to further self-assemble chiral molecules into nanostructures. Phthalocyanine, hexabenzocoronene, and perylene are typical samples for discotic molecules. Engelkamp et al. [63] reported that the phthalocyanine derivative bearing four benzo crown ether moieties with optically active tails self-assembles into long columns driven by π–π stacking interactions in chloroform, resulting in the formation of fibers with a right-handed helix as evidenced by the appearance of circular dichroism spectra. The fibers further assemble into superhelices with an opposite left-handed helix to that of each fiber, as demonstrated by TEM observations of the helical aggregates. This process is a typical example of the hierarchical self-assembly of small components into a complex architecture with helical chirality.

Comparing with the discotic molecules with symmetric geometry, asymmetric amphiphiles normally can get better controllability regarding of their self-assembly behavior. Aida's group [54] has fabricated a series of helical supramolecular structures in hydrogels using gemini-shaped, chiral amphiphilic hexa-*peri*-hexabenzocoronene (HBC) (Figure 1, top). When the concentration of amphiphilic molecule (*S*)-**2** in 2-methyltetrahydrofuran (MeTHF) was higher (3 mg mL^{-1}), a gelatinous suspension resulted (Figure 1(a)). Fluorescence microscopy of the suspension, after being cast on a glass substrate, showed the presence of several tens of micrometer-long fibers (Figure 1(b)). Transmission electron microscopy (TEM) of an air-dried suspension (Figure 1(c)) demonstrated that these fibers are tubular, having a uniform diameter of 20 nm with a wall thickness of 3 nm. These results are analogous to the assembling behaviors observed for achiral HBC amphiphile **1** [64] and the enantiomer (*R*)-2 (Figure 1, top). In sharp contrast, chiral HBC amphiphile **3** bearing branched asymmetric centers in the paraffinic side chains did not give nanotubular assemblies but irregular aggregates in a hot MeTHF. The authors considered that the failure of the nanotube formation chiral HBC amphiphile **3** was most likely because of its branched paraffinic side chains that prevent the formation of a bilayer tape.

Recently, an asymmetric sugar-based amphiphilic perylene diimide derivative *N*-(1-hexylheptyl)-*N*'-((4-aminophenyl)-α-*D*-gluco-pyranoside)-perylene-3,4,9,10-tetracarboxylbisimide (PTCDI-HAG, Figure 2) was synthesized in our lab and its aggregate morphologies in different solvents with varying volume ratios were studied by cooperative of the interactions between the π–π stacking and hydrogen bond [56]. We have demonstrated PTCDI-HAG

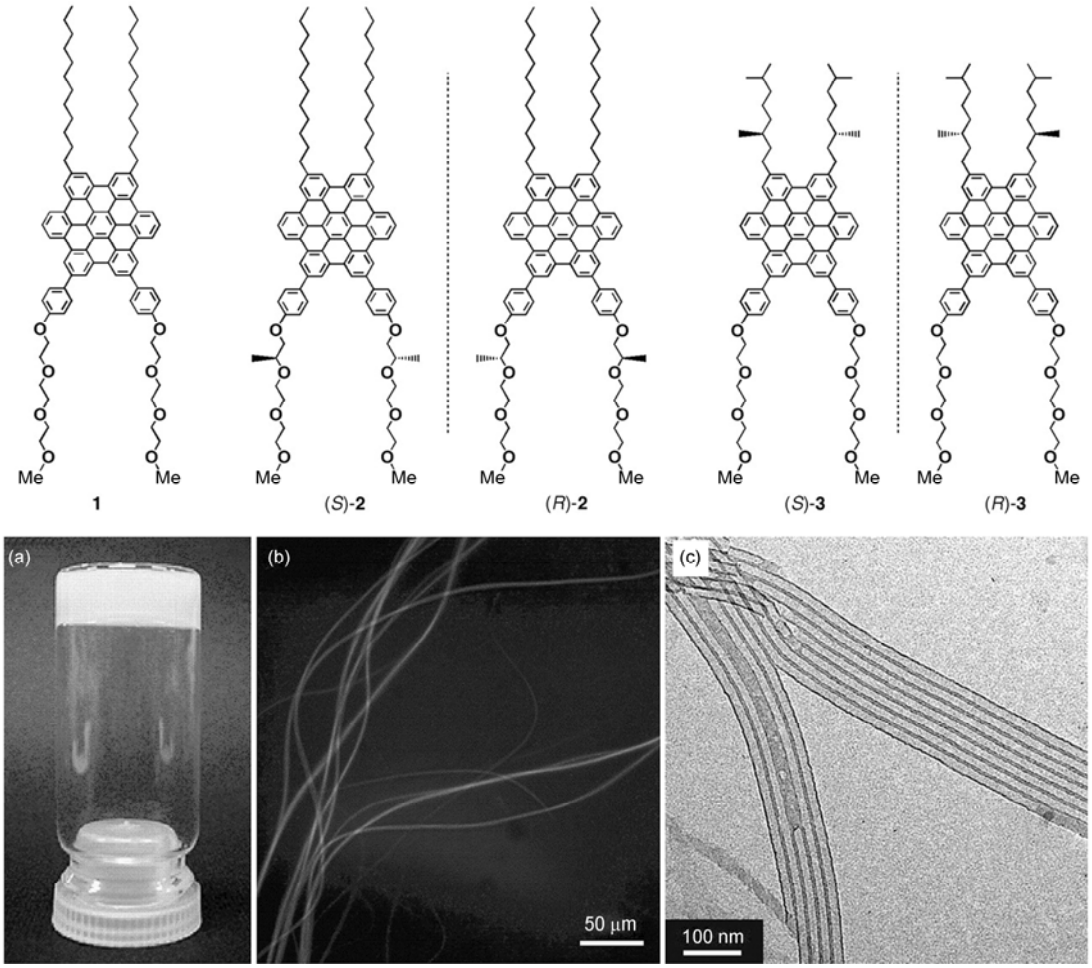

Figure 1 Molecular structures of HBC amphiphiles **1**–**3** (top), and self-assembly of chiral HBC amphiphile **2** (bottom). (a) A gelatinous suspension formed at 20°C upon slow cooling of a hot MeTHF solution of chiral HBC amphiphile (*S*)-**2** (3 mg mL^{-1}). (b) Fluorescence micrograph of fibers formed at 20°C upon slow cooling of a hot MeTHF solution of (*S*)-**2** (1 mg mL^{-1}). (c) TEM micrographs of nanotubes formed from chiral HBC amphiphile (*S*)-**2** in MeTHF. Reprinted with permission from ref. [54], Copyright 2005, National Academy of Sciences.

molecules adopted a left-handed (i.e. counter-clockwise) helical arrangement during aggregation in $CHCl_3$/*n*-C_8H_{18} as evidenced by the appearance of circular dichroism spectra (Figure 2(a)), but adopted a right-handed helical arrangement in THF/H_2O (Figure 2(b)). Correspondingly, one-dimensional left-handed helical nanowires of PTCDI-HAG in $CHCl_3$/*n*-C_8H_{18} (Figure 2(c)) and right-handed helical fibers in THF/H_2O (Figure 2(d)) were obtained.

1.2 Rod-like π-conjugated molecules as tectons

Comparing with planer macrocyclic aromatic molecules, the properties of rod-like π-conjugated molecules are much easier to be tuned by changing the numbers of repeating units of oligomers. For instance, the absorption spectra can be tuned from 400 to 900 nm by changing the number of repeating unit of oligothiophene. Moreover, the π–π stacking interactions will also be tuned by changing the number of repeating units, which give a high possibility to tune the function and structures of supramolecular structures.

Meijer and co-workers [65,66] studied the self-assembly of linear chiral amphiphilic thiophenes containing ethylene oxide side chains in solution and in the solid state in collaboration with the group of Lazaronni and the group of Feast (Figure 3). Based on circular dichroism studies, in polar solvents like *n*-butanol and water chiral aggregates are formed which are not fiber-like. Remarkably, when deposited from molecularly dissolved solutions like THF or toluene helical fibers were obtained. On graphite nanowires were formed while on mica platelets were generated. Surprisingly both thiophene enantiomers formed left-handed helices on silicon while the CD measurements on these dropcast films revealed mirror images for both enantiomers. This observation was dependent on the hydrophilicity of the silicon. Furthermore, the achiral sexithiophene, lacking the methyl group at the asymmetric center, did not form helical aggregates.

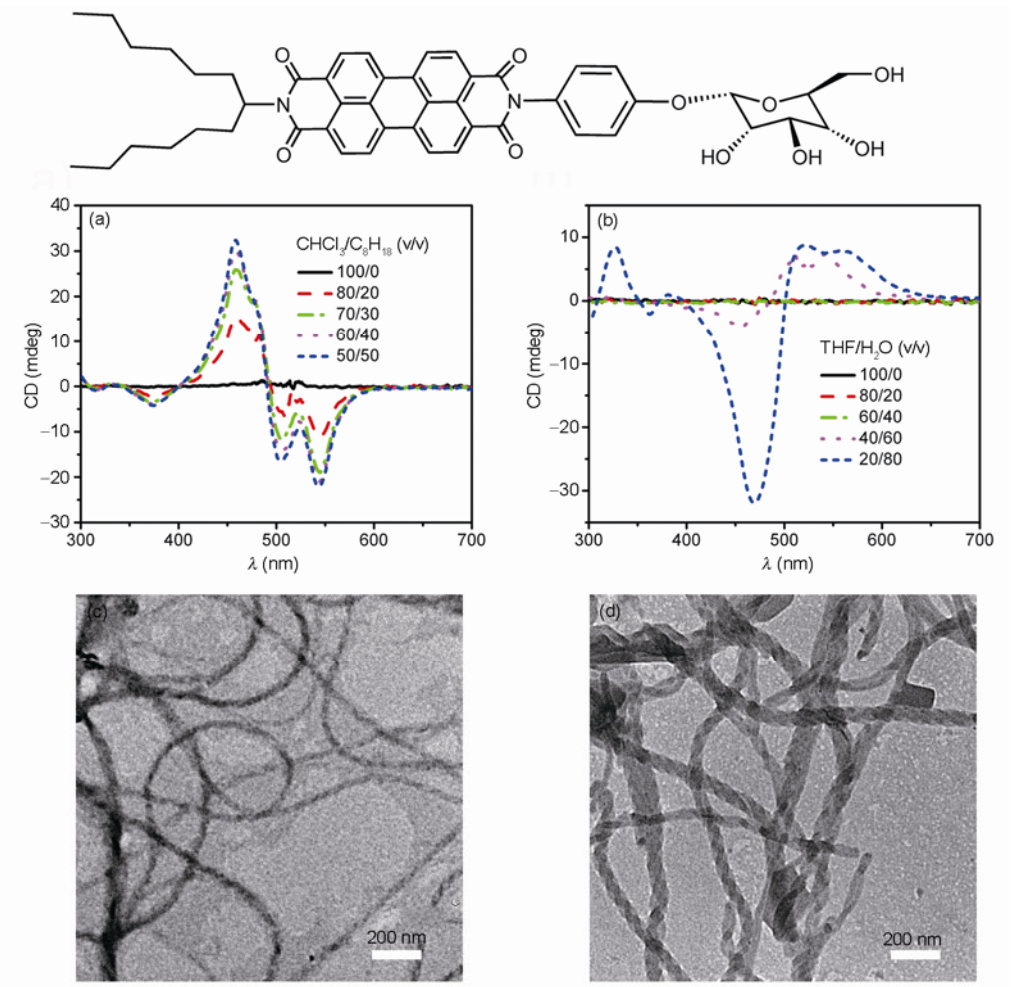

Figure 2 Chemical structure of the PTCDI-HAG amphiphile molecule. Circular dichroism (CD) spectra of the PTCDI-HAG molecules in different volume ratios of (a) $CHCl_3$/*n*-C_8H_{18} or (b) THF/H_2O and TEM images of the PTCDI-HAG helical nanowires obtained from (c) chloroform/*n*-octane (50/50, v/v) and (d) THF/H_2O (50/50, v/v). Reprinted with permission from ref. [56], Copyright 2011, RSC Publishing.

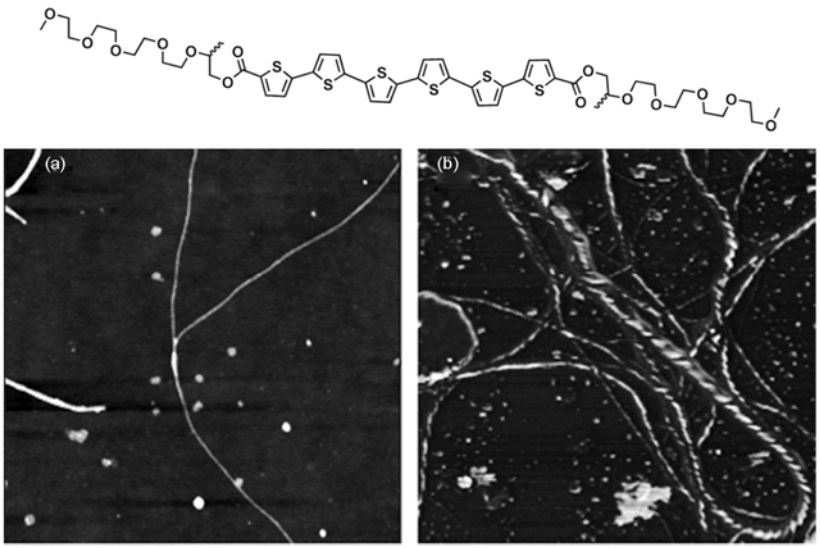

Figure 3 Chiral oligothiophenes(top), (a) and (b) equipped with ethylene oxides forming nanowires on silicon. Reprinted with permission from ref. [66], Copyright 2004, American Chemical Society.

Another typical rod-like chiral amphiphiles oligo (*p*-phenylene vinylene) (OPV) was synthesized by Meijer and Würther et al. [67]. Interestingly, a complex consisted of donor (OPV)-acceptor (perylene bisimide)-donor triads (Figure 4) was created and studied. This supramolecular structure is formed in a hierarchical process in which the hydrogen-bonded triad further self-assembles in one dimension by π–π interactions. The resulting J-type aggregates are characterized by bathochromic shifts for both chromophores, as high as 40 nm for the perylene moiety. The chirality of the OPV side chains imparts chirality to the aggregates as well and is transferred to the perylene bisimide as observed with CD spectroscopy. From fluorescence and photoinduced absorption measurements it can be concluded that within the aggregates photoinduced electron transfer occurs from the OPVs to the perylene bisimide. Moreover, the optical techniques prove the existence of two phases for the hydrogen-bonded complex in solution, namely, a molecularly dissolved one at high temperatures and an aggregated state at low temperatures. A sharp transition between the two states is observed at 55°C (10^{-5} mol/L in MCH). Atomic force microscopy (AFM) measurements using this molecule on glass clearly show rod like aggregates consisting of left-handed helical π–π co-aggregates of the two dyes that are further assembled to right-handed nanometer-scale supercoils (Figure 4).

1.3 Other functional π-conjugated molecules as tectons

Besides the discotic and rod-like chiral amphiphiles discussed above, 1,1′-bi-2-naphthol (BINOL) and its derivatives [62] have generated particular interest because of their stable chiral configuration and highly tunable structure. More importantly, the fluorescent properties of BINOL can be systematically varied by structural modification, which can lead to its extensive application in molecular recognition and fluorescent sensors as the detailed elucidation in next section.

Recently, the self-assembly of Schiff-based chiral amphiphiles have been paid more and more attention. Compared with planar and linear π-conjugated chiral molecules, Schiff-based chiral amphiphiles are easy to prepare, and self-assembly of these molecules can also give rise to fascinating aggregate having stable morphologies. More important, some group such as azobenzene can be introduced to these chiral amphiphiles, which may lead to some functional materials with novel optoelectronic properties. Hsu and co-workers [68–70] have made significant contributions to the design of self-assembled helical structures of sugar-appended Schiff base chiral rod-coil amphiphiles. They have synthesized a series of sugar-appended chiral rod-coil amphiphiles (Figure 5) and their self-assembled behaviors in solution, especially, the effect of the variation of the helical twisting power (HTP) on the morphologies of self-assembled aggregation, was investigated in detail [68].

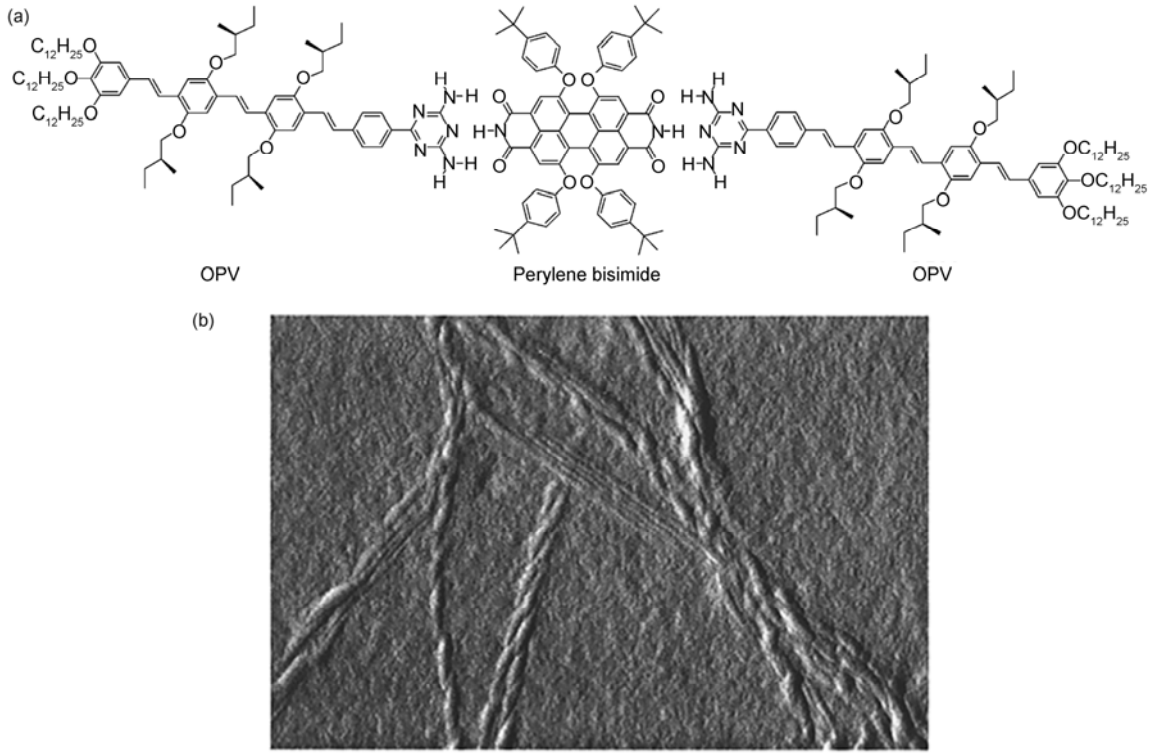

Figure 4 The supramolecular donor-acceptor-donor triads (a) and self-assembled helical nanostructure (b) in apolar solvent (MCH). Reprinted with permission from [67], Copyright 2002, American Chemical Society.

The HTP induced by chiral sugar in the self-assembled helical morphology was dependent upon the alkoxy chain length. Increasing the alkoxy chain length caused the self-assembled morphology to change from platelet-like texture to helical-twist morphology with varying pitch length and then revert to the platelet-like texture (Figure 5). The transformation from platelet-like to helical-twist morphology is induced by significant steric hindrance, when the effective size of adjacent alkoxy chains reaches the threshold of helical twisting and bending, resulting in the formation of a chiral smectic C phase. However, as the alkoxy chain length increases further, the disordering of the alkoxy chain conformation in the smectic-like layered structure may give rise to a structural imperfection that reduces the steric-hindrance effect. Eventually, the steric-hindrance effect may reach a compromise with the structural imperfection to produce a platelet-like morphology, leading to the formation of a low-order smectic phase.

To encode the cooperative contribution of different groups on the molecular self-assembly, Huang's group [8, 71] designed an amphiphile C_4AG that was composed of three parts: butyl, azobenzene group, and sugar moiety (Figure 6(a)). This molecule can self-assemble into double helices in water and form viscoelastic hydrogels. This self-assembly process is so delicate that replacement of any part of these three groups failed to provide one-dimensional self-assembly (Figure 6(b) and (c)). Helical nanofibers cannot be observed when the azobenzene group is replaced by a saturated aliphatic chain. It is therefore suggested that π–π stacking of the azobenzene groups was crucial for the formation of one-dimensional helices. When the sugar head was replaced by another hydrophilic group, the amphiphilies

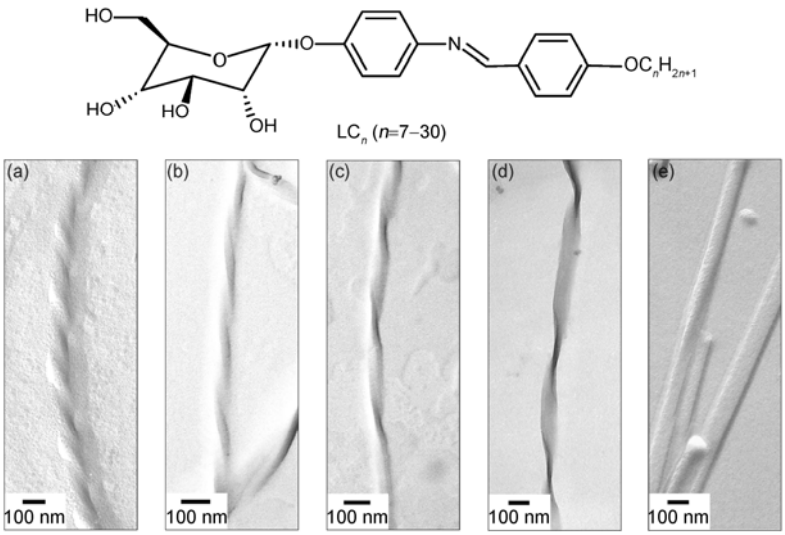

Figure 5 Chemical structure of the sugar-appended schiff base chiral rod-coil amphiphiles (top) and TEM images of the hierarchical superstructures of (a) LC_{14}, (b) LC_{16}, (c) LC_{18}, (d) LC_{22}, and (e) LC_{30} self-assembled in solution at ambient temperature. Reprinted with permission from ref. [68], Copyright 2008, American Chemical Society.

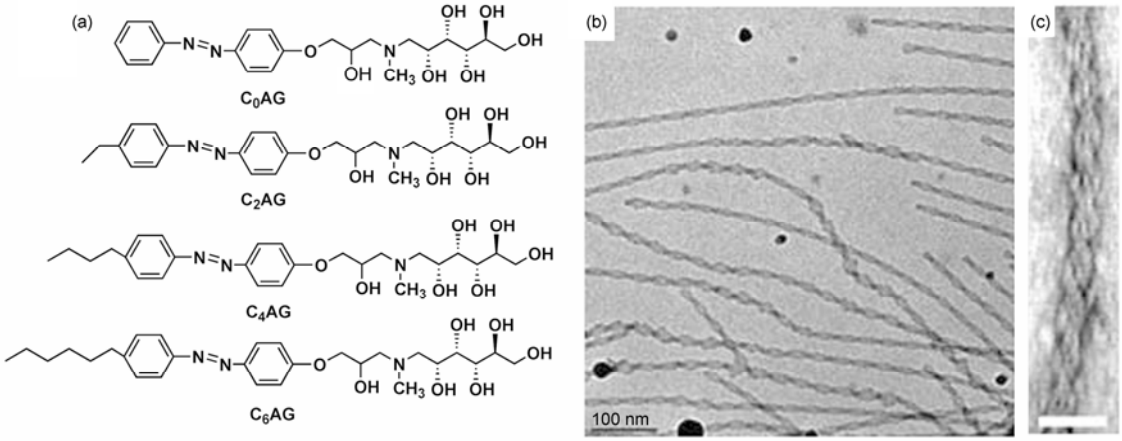

Figure 6 (a) Molecular structure of C_4AG amphiphile and its analoges; (b) cryo-TEM image of a C_4AG double helix in solution; (c) TEM image of double helix stained with uranyl acetate (scale bar is 50 nm). Reprinted with permission from ref. [71], Copyright 2010, RSC Publishing.

would self-organize into global micelles or vesicles but not one-dimensional architectures. This means that the multiple hydrogen-bonds generated between the sugar heads can guide the orientation of molecules within aggregates. In addition, the multiple hydrogen bonds in the sugar moiety have produced a steric effect that leads to the formation of twisting in the structures. Furthermore, the butyl chain or longer hydrocarbon chain in the molecule was proved to be essential for the one-dimensional nanostructure, since without it, or with shorter chains, only irregular precipitates are formed. This indicates that the rigid molecules such as C_0AG and C_2AG tend to closely pack via π–π stacking, forming precipitates. However, the steric hindrance of the association of hydrophobic butyl or hexyl groups can interfere with the close packing between aromatic groups so that precipitates are avoided.

With more and more chiral amphiphiles developed for self-assembly, some new molecules with novel structure was designed and synthesized. In a recent example, Lee and co-workers [72] have studied the aqueous self-assembly of a laterally grafted bent-rod amphiphile **1** comprising a meta-linked oligoparaphenylene (OPP)-based segment functionalized with nitrile groups and a chiral oligoether dendron side chain (Figure 7(a)). Amphiphile **1** self-assembles in water into nanotubular aggregates with a uniform diameter of 6.5 nm and lengths of several micrometers. The cylinders have a hollow interior with a diameter of 3 nm, as demonstrated by TEM experiments. Molecular dynamics revealed that six molecules of **1** are arranged in a single slice yielding a hexameric macrocycle stabilized by electrostatic interactions between the nitrile and phenoxy groups (Figure 7(a)). Further interaction between adjacent hexameric slices through π-stacking and electrostatic interactions with a rotation of 16.5° between each segment leads to the formation of helical tubules (Figure 7(a)). Interestingly, the presence of nitrile groups in the internal cavity of the tubules was exploited to bind silver salts through nitrile-silver interactions. Dynamic light scattering, AFM, CD and TEM experiments demonstrate that the addition of up to 10 equivalents of silver dodecylsulfate (AgDS) gives rise to the dissociation of the initial chiral nanotubes into segmented tubes (toroids) that maintain the initial helical order (Figure 7(b)).

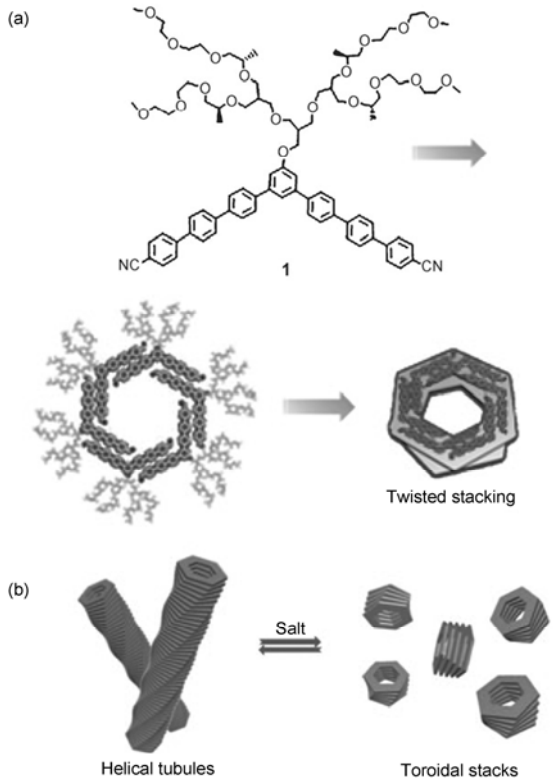

Figure 7 Schematic representation of (a) helical stacking of hexameric macrocycles and (b) dissociation into toroidal stacks. Reprinted with permission from ref. [72], Copyright 2010, Wiley-VCH.

2 Functions and applications of chiral supramolecular nanostructures

So far, many supramolecular nanostructures based on the chiral amphiphiles with π-conjugated tectons, especially fibrils, nanobelts or nanoribbons, nanotubes, as well as a variety of helical structures, have been successfully fabricated. Meanwhile, with the purpose of fabrication of well designed and smart materials, there is a lot of effort aimed at their potential applications. In the following we will give a brief overview of the progress in this aspect.

2.1 Chiral recognition

In recent years, the development of fluorescent sensors for the enantioselective recognition of chiral organic molecules has received increasing attention. These sensors can potentially provide a real-time technique to determine the enantiomeric composition of chiral organic compounds which could greatly facilitate the high throughput screening of chiral catalysts and reagents and allow rapid assay of chiral molecules. Pu [62] has studied the use of the BINOL-based fluorescent sensors for the recognition of amines, amino alcohols, α-hydroxycarboxylic acids and amino acid derivatives, and have achieved both high enantioselectivity and sensitivity in a number of cases. The research on the BINOL-based molecules has demonstrated that it is possible to develop enantioselective and sensitive fluorescent sensors for the chiral assay of organic molecules by designing and systematically modifying the structure of the chiral molecular receptors and shown great potential for the development of rapid assays of chiral organic compounds. Moreover, BINOL-based molecules can also be applied in asymmetric catalysis, and the detailed report can be found in reference [73].

2.2 Anisotropic electrical conduction

Polycyclic aromatic hydrocarbons (PAHs) are considered as one of the promising components for molecular electronics

because of their strong tendency to form one-dimensional columnar structures via π-stacking interactions. Some unidirectionally assembled PAHs have been shown to exhibit anisotropic charge- and energy-transport activities. A representative example of anisotropic electrical conduction was reported by Adia's group [55]. Firstly, well-defined nanotubular objects were obtained by dissolving Gemini-shaped HBC amphiphiles (*S*)-**2** (Figure 1) in a hot MeTHF solution (1.5 mg mL^{-1}), Then, a glass hook was dipped into this suspension to collect the nanotube bundles and then pulled up to stretch the captured aggregate. Polarized optical microscopy of a macroscopic fiber of (*S*)-**2** (Figure 8(a), (b)) and small angle X-ray diffraction analysis suggested that the majority of the nanotube bundles are oriented unidirectionally along the fiber axis. When doped with I_2, the fiber rapidly turned from yellow to dark brown. Electron spin resonance (ESR) spectroscopy of the resulting fiber displayed a signal with a *g* value of 2.00256 at 296 K (Figure 8(c)), indicating the generation of radical species as charge carriers. Quantitative ESR analysis, using diphenylpicrylhydrazyl as a reference, showed that one charge carrier is generated per 10–11 HBC molecules after the intensity of the ESR signal reached a constant value. Upon doping with I_2, ρ_{II} (resistivities along) suddenly dropped and reached a constant value of 20 Ω cm at 300 K after 1 h. Likewise, $\rho_{\perp}$ (resistivities across) decreased upon doping with I_2, however, the final value of $\rho_{\perp}$ (280 Ω cm at 300 K) was more than an order-of-magnitude larger than $\rho_{//}$ ($\rho_{\perp}/\rho_{//} = 14$). Upon cooling, ρ_{II} and$\rho_{\perp}$ both increased, indicating a semiconducting character (Figure 8(d)). The difference between $\rho_{//}$ and $\rho_{\perp}$ increased at lower temperatures, and a ratio $\rho_{\perp}/\rho_{//}$ of 35 was observed at 55 K. The anisotropic conduction in the fiber was also confirmed by flash-photolysis time-resolved microwave conductivity measurements. This conductive nanotubes with one-handed helical chirality are expected to permit the realization of nanometer-scale solenoids.

2.3 Switchable interfaces

Amphiphilic molecules contain both hydrophilic and hydrophobic parts. When amphiphiles are dispersed in solvent, the hydrophilic component of the amphiphile preferentially interacts with the aqueous or polar phase while the hydrophobic portion tends to reside in the air or in the nonpolar solvent. Therefore, some supramolecular nanomaterails with switchable interfaces can be obtained by elegantly changing the arrangement of amphiphiles in different solvent systems. Recently, our group [56] reported the self-assmebly of a new sugar-based amphiphilic perylene diimide derivative PTCDI-HAG (Figure 2) in chloroform/*n*-octane and THF/H_2O. We have demonstrated the formation of one-dimensional left-handed helical structures in chloroform/*n*-octane and right-handed helical structures in THF/H_2O for PTCDI-HAG molecules. However, significant differences lie in the arrangement of the molecules in the two oppositely handed nanowire systems. As far as the left-handed nanowires obtained from chloroform/*n*-octane are concerned, the galactosyl group is buried inside the aggregates to form a hydrophilic core that is sheltered from octane. The 1-hexylheptyl chains tend to gather on the

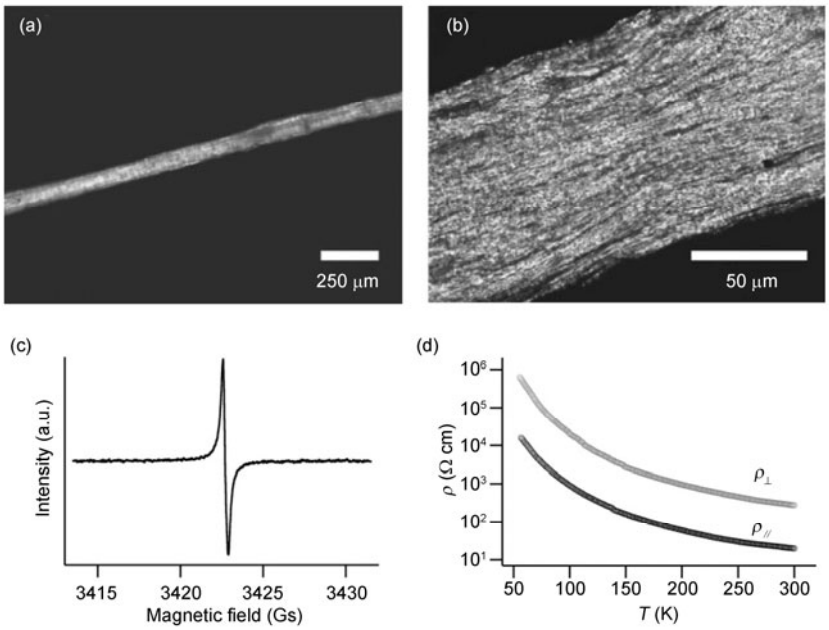

Figure 8 (a) A polarized optical microscopy image, (b) a magnified image of a macroscopic fiber consisting of bundled nanotubes of (*S*)-**2**, (c) X-band ESR spectrum at 296 K (microwave frequency of 9.5 GHz) of an I_2-doped macroscopic fiber consisting of bundled nanotubes of (*S*)-**2**, and (d) temperature dependencies of its resistivities along ($\rho_{//}$) and across ($\rho_{\perp}$) the fiber axis. Reprinted with permission from ref. [55], Copyright 2006, Wiley-VCH.

outside to stabilize the aggregates in octane. Compared to the molecular arrangement in the chloroform/*n*-octane, the amphiphile molecules have an opposite arrangement in polar THF/H_2O, that is, galactosyl groups are presented to the outside of the amphiphilic aggregates. Solvent molecules can therefore modulate the supramolecular arrangement of the perylene amphiphiles in the nanowires, as shown in the schematic representation in Figure 9(a). To further validate our arguments, the contact angles of films consisting of the helical nanowires were examined. The contact angle of the helical nanowires from chloroform/*n*-octane is $126^{o}\pm5^{o}$ (Figure 9(b)), clearly indicating its hydrophobic nature. On the other hand, the contact angle of nanowires prepared from THF/H_2O was $35^{o}\pm5^{o}$ (Figure 9(c)), indicating its hydrophilic nature. These results further confirm the supramolecular arrangement as suggested in Figure 9(a), and provide new pathways to the preparation of switchable interfaces based on designed supramolecular interactions.

2.4 Soft template

One of the primary goals of creating one-dimensional soft supramolecular assemblies is for the template-synthesis of one-dimensional hard materials since these materials are found to have great potential in optical materials due to their specific surface effect. So far, there are some nice examples that utilize this method to produce interesting one-dimensional hard nanomaterials. For example, Huang's group [73] reported the fabrication of SiO_2 nanomaterials with sugar based amphiphiles as a template. When tetraethyl orthosilicate (TEOS) is used as the source of silica, hydrogen bond formation is possible between TEOS and the sugar based surfactant, like C_4AG (Figure 6). In this way, TEOS was effectively adsorbed to the surface of the double helices formed by C_4AG, which allows for the formation of delicate double helical SiO_2 nanotubes)[69]. Interestingly, upon decoupling the double helices by addition of CTAB to the C_4AG system, single helical SiO_2 nanotubes can be obtained as well. In the later case, the silica source might be adsorbed to the single helical C_4AG template by electrostatic force between the positively charged CTAB, and possible scheme of helical SiO_2 nanomaterials in the system of C_4AG/CTAB presented in Figure 10 [74].

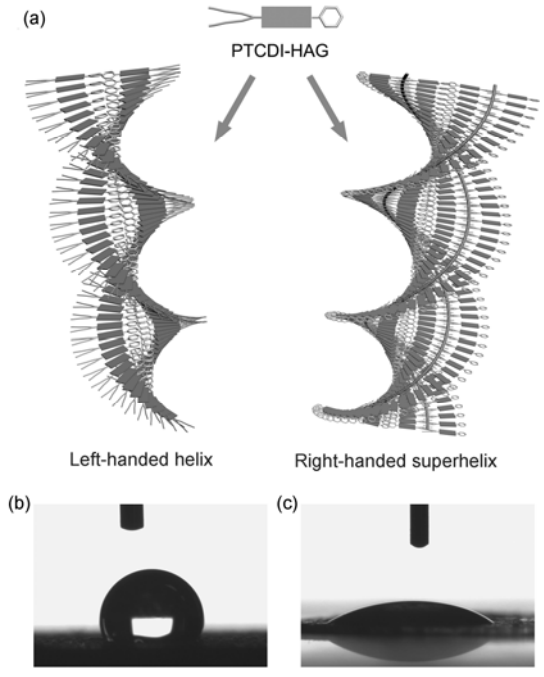

Figure 9 (a) Schematic representation of the self-assembly process of the PTCDI-HAG helical nanowires; (b) contact angles of the film that consists of the helical nanowires obtained from (b) chloroform/*n*-octane ($126^{o}\pm5^{o}$) and (c) THF/H_2O ($35^{o}\pm5^{o}$). Reprinted with permission from ref. [56], Copyright 2011, RSC Publishing.

3 Summary and perspectives

This review has summarized the recent development of supramolecular self-assembly of chiral amphiphiles with π-conjugated techons on the basis of experimental exploration by elegantly utilizing cooperative noncavent forces such as π–π stacking, hydrophobic interaction, hydrogen bond and electrostatic interaction. Well-defined helical nanotubes, nanofibers and nanowires based on these chiral amphiphiles can be obtained in solution or at surface. The potential applications of these self-assembled helical nanostructures in chiral recognition, asymmetric catalysis, electrical conduction, switchable interfaces and soft template for the fabrication of one-dimensional hard materials are described by a representative example. It is hoped that this review can provide a macroscopical strategy for the construction of self-assembling soft materials by rational design.

With more and more chiral amphiphiles developed for

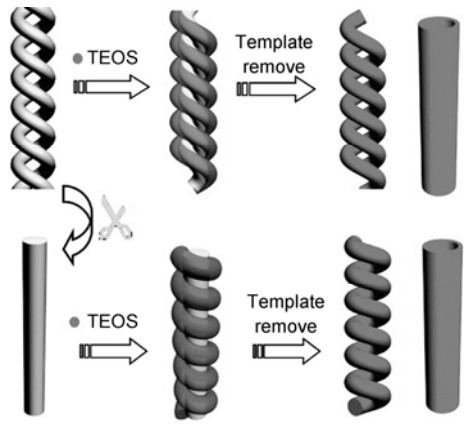

Figure 10 Possible scheme of helical SiO_2 nanomaterials in the system of C_4AG/CTAB. The brown ribbon on the C_4AG/CTAB fiber gives a proposed location of CTAB, which can not be observed under TEM. Reprinted with permission from ref. [74], Copyright 2010, American Chemical Society.

self-assembly, we should not forget that some basic challenges still remain unsolved. First, the amount of chiral amphiphiles with π-conjugated systems available to self-assembly is very limited due to the difficulties in the designing and synthesis of novel chiral amphiphiles. Second, helical nanostructures are not prepared without difficulty. The design and reproducible preparation of helical nanostructures can present a significant challenge, especially since slight changes in the structures of the molecular building blocks used and the methods by which the nanofibers are assembled can affect the supramolecular structure enormously. Finally, the relationships between self-assembled nanostructures and function should be further revealed, especially for one-dimensional helical nanostructures. Clearly this will be important for the further application of supramolecular materials in the biological, physical, and materials sciences.

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